

☐ JP02064140

WPIDS  
1990-068671-[Full Text](#)

**Styrene -based polymer compsn. and stretched moulding - has improved mechanical properties and solvent resistance, contains poly phenylene ether.**

Patent Number EP 356857 A 7 March, 1990

**Abstract**

EP 356857 A UPAB: 13 October, 1994

(I) A styrene-based polymer compsn. comprises (A) 10-98 weight% of a styrene based polymer having syndiotactic configuration with a racemic pentad of 30% or more and (B) 90-2 weight% of a polyphenylene ether having an intrinsic viscosity of 0.28 dl/g or more at 30 deg.C in chloroform. (II) A styrene-based polymer compsn. comprises (A) and (B) above with (C) 3-40 pts.weight of a flame retarder (pref. at least one of decabromodiphenyl ether, polytribromostyrene and poly (dibromophenylene oxide) and (D) 1-15 pts.weight of a flame retardant aid (pref. antimony trioxide) based on 100 pts.weight of (A)+(B) (III) A styrene-based polymer compsn. comprises (A) and (B) above with (E) 5-85 pts.weight of a rubber-like elastomer (pref. containing a styrene-based cpd. as a partial component thereof) and/or 1-250 pts.weight of an inorganic filler (pref. glass fibre) based on 100 pts.weight (A)+(B). (IV) a styrene-based polymer compsn. comprises (A), (B), (C), (D) and (E) above. (V) A stretched moulding which comprises stretching the styrene-based polymer in (I) above (pref. with a draw ratio at least in uniaxially stretching of at least 1.5 times, or a draw ratio in biaxially of at least 1.2 times in each direction) is also claimed.

(VI) Production of a stretched moulding comprises heat melting the compsn. of (I) above, cooling the resultant molten compsn. to a temperature lower than a temperature 30 deg.C above the glass transition temperature of the compsn. to form a raw sheet, and then subjecting the sheet to stretching treatment with heating to a temperature between the glass transition temperature and a m.pt. of the compsn. (VII) production of a stretched moulding comprises subjecting the moulding in (V) above to annealing at a temperature between 100 deg.C and the m.pt. of the compsn.

ADVANTAGE - This moulding has improved mechanical properties. 0/0  
Dwg.0/0

**Inventor(s)**

AKIKAZU, N; KEISUKE, F; KOMEI, Y; TAKASHI, S

**Assignee(s)**

(IDEK) IDEMITSU KOSAN CO LTD

**Application Information**

EP 1989-115354 19 August, 1989

**Priority Information**

JP 1988-215095 31 August, 1988  
JP 1988-244581 30 September, 1988  
JP 1988-244583 30 September, 1988

**Patent Information**

Number	Kind	Date	Application	Date
(1) EP 356857	A	7 March, 1990	EP 1989-115354	19 August, 1989
JP 02064140	A	5 March, 1990	JP 1988-215095	31 August, 1988
AU 8940896	A	8 March, 1990		
JP 02092948	A	3 April, 1990	JP 1988-244583	30 September, 1988
FI 8904030	A	1 March, 1990		
JP 02218724	A	31 August, 1990	JP 1988-244581	30 September, 1988

Number	Kind	Date	Application	Date
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TW 209876	A	21 July, 1993	TW 1991-107828	14 August, 1989
(2) EP 356857	B1	30 November, 1994	EP 1989-115354	19 August, 1989
DE 68919591	E	12 January, 1995	DE 1989-619591	19 August, 1989
TW 269702	A	1 February, 1996	TW 1993-104606	14 August, 1989
JP 2636900	B2	30 July, 1997	JP 1988-244581	30 September, 1988
JP 2824067	B2	11 November, 1998	JP 1988-244583	30 September, 1988
KR 9606158	B1	9 May, 1996	KR 1989-12716	31 August, 1989
KR 9606160	B1	9 May, 1996	KR 1996-3815	16 February, 1996

(1) - **R:** AT BE CH DE ES FR GB IT LI NL SE

(2) - **R:** AT BE CH DE ES FR GB IT LI NL SE

☐ JP02092948

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ADVANTAGE - This moulding has improved mechanical properties. 0/0  
Dwg.0/0

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ADVANTAGE - This moulding has improved mechanical properties. 0/0  
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WPIDS  
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Dwg.0/0

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□ JP02218724

WPIDS  
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Dwg.0/0

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**Assignee(s)**

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(2) - **R:** AT BE CH DE ES FR GB IT LI NL SE

**Stereospecific polystyrene production - by using catalyst comprising cyclopentadienyl titanium halide and at least one alumoxane cpd..**

Patent Number JP 63268709 A 7 November, 1988

**Abstract**

JP 63268709 A UPAB: 23 September, 1993

Stereospecific polystyrene is produced by the use of catalyst comprising (A) Ti cpd. of formula  $Cp_2TiX_2$  (I) and (B) at least one alumoxane of formula (II) or (III). In the formulae, Cp = cyclopentadienyl gp.; X = halogen; R= CH<sub>3</sub> or ethyl; n = 1-40.

Ti cpd. includes pref. bis(cyclopentadienyl)titanium dichloride (A) is used pref. as hydrocarbon solution (B) is prepared pref. by hydrolysing slowly trialkylaluminium with crystal water e.g. copper sulphate hydrate. The catalyst and inert hydrocarbon solvent e.g. hexane, benzene are supplied to reactor and styrene is fed into the system under inert gas and polymerised at room temperature to 90 deg.C.

ADVANTAGE - Syndiotactic polystyrene is obtd. The raw materials for the catalysts are available.  
0/0

**Assignee(s)**

(ASAH) ASAHI CHEM IND CO LTD

**Application Information**

JP 1987-101783 27 April, 1987

**Priority Information**

JP 1987-101783 27 April, 1987

**Patent Information**

Number	Kind	Date	Application	Date
JP 63268709	A	7 November, 1988	JP 1987-101783	27 April, 1987

☐ JP09052958

WPIDS  
1997-197301-Full Text

**Forming resin moulding with good surface appearance - comprises melting compsn. containing styrene polymer having syndiotactic stereospecificity and thermoplastic resin or elastomer having segment miscible with amorphous phase of styrene polymer.**

Patent Number JP 09052958 A 25 February, 1997

**Abstract**

JP 09052958 A UPAB: 2 May, 1997

Forming resin moulding comprises: (i) melting a resin compsn. consisting of: (A) 99-1 weight% of styrene polymer having syndiotactic stereospecificity; and (B) 1-99 weight% of one or more thermoplastic resins or elastomers consisting of segment miscible with amorphous phase part of component (A); at 270-370 deg. C; and (ii) moulding it using a mould having a mould cavity coated with a heat insulating material of not more than 0.01 cal.cm.-sec- deg. C thermal conductivity at 20 deg. C while holding the wall temperature of the mould cavity at 20-150 deg. C.

ADVANTAGE - Resin mouldings have good heat and chemical resistance, and surface appearance can be efficiently obtd.. Dwg.0/0

**Assignee(s)**

(ASAH) ASahi KASEI KOGYO KK

**Application Information**

JP 1995-204276 10 August, 1995

**Priority Information**

JP 1995-204276 10 August, 1995

**Patent Information**

Number	Kind	Date	Application	Date
JP 09052958	A	25 February, 1997	JP 1995-204276	10 August, 1995

☐ JP08143699

WPIDS  
1996-319042-Full Text

**Fine porous film mfr. for filters - comprising moulding molten styrene -type polymer and miscible polymer in film form and extracting with solvent..**

Patent Number JP 08143699 A 4 June, 1996

***Abstract***

JP 08143699 A UPAB: 19 August, 1996

Mfg. fine porous film of styrene type polymer having syndiotactic structure comprises moulding the molten styrene polymer and homogeneously miscible polymer into a film form and extracting part of the polymers forming the filmy substance with solvent.

USE - The film is useful for e.g. ultrafilter or separation film.

ADVANTAGE - Fine porous film can be simply obtd. from styrene type polymer having syndiotactic structure by melt-moulding. Dwg.0/0

***Assignee(s)***

(ASAH) ASAHI KASEI KOGYO KK

***Application Information***

JP 1994-289499 24 November, 1994

***Priority Information***

JP 1994-289499 24 November, 1994

***Patent Information***

Number	Kind	Date	Application	Date
JP 08143699	A	4 June, 1996	JP 1994-289499	24 November, 1994

☐ JP60079005

WPIDS  
1984-196347-Full Text

**Selective hydrogenation of conjugated diene units in polymer - using catalyst containing di  
cyclopentadiene- titanium cpd. and hydrocarbon-lithium cpd..**

Patent Number DE 3401983 A 2 August, 1984

**Abstract**

DE 3401983 A UPAB: 16 November, 1993

Double bonds in conjugated diene units in polymers obtd. by (co)polymerisation of conjugated dienes, are selectively hydrogenated with H<sub>2</sub> in an organic solvent, using a catalyst comprising (A) a dicyclopentadienyl-Ti cpd. of formula (C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>TiRR', and (B) a hydrocarbon-Li cpd. If the (co)polymer is a living polymer containing Li in the polymer chain, component (B) may be (partly) omitted. R, R'=1-8C alkyl or alkoxy, 6-8C aryl, aryloxy, aralkyl or cycloalkyl, halogen or carbonyl.

ADVANTAGE - Catalyst has high activity and selectivity and good reproducibility. Mild conditions are used. Living polymers can be hydrogenated continuously in the reactor in which they are prepared Resistance to weathering, oxidation and heat is improved. Dwg.0/0

**Inventor(s)**

KISHIMOTO, Y; MORITA, H

**Assignee(s)**

(ASAHI) ASAHI KASEI KOGYO KK

**Application Information**

DE 1984-3401983 20 January, 1984

**Priority Information**

JP 1983-6718 20 January, 1983

JP 1983-186983 7 October, 1983

**Patent Information**

Number	Kind	Date	Application	Date
DE 3401983	A	2 August, 1984	DE 1984-3401983	20 January, 1984
GB 2134909	A	22 August, 1984	GB 1984-305	6 January, 1984
FR 2539745	A	27 July, 1984	FR 1984-820	19 January, 1984
JP 59133203	A	31 July, 1984	JP 1983-6718	20 January, 1983
US 4501857	A	26 February, 1985	US 1984-568692	6 January, 1984
JP 60079005	A	4 May, 1985	JP 1983-186983	7 October, 1983
GB 2134909	B	20 August, 1986	GB 1984-305	6 January, 1984
JP 63004841	B	1 February, 1988		
JP 63005401	B	3 February, 1988		
DE 3448317	A	2 February, 1989	DE 1984-3448317	20 January, 1984
DE 3401983	C	8 March, 1990	DE 1984-3401983	20 January, 1984
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US 4501857	A	26 February, 1985	US 1984-568692	6 January, 1984
JP 60079005	A	4 May, 1985	JP 1983-186983	7 October, 1983
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**EUROPEAN PATENT APPLICATION**

21 Application number: 89115354.6

22 Date of filing: 19.08.89

51 Int. Cl.<sup>5</sup>: **C08L 25/06 , C08L 71/12 ,  
 B29C 55/00 , C08J 5/18 ,  
 //(C08L25/06,71:12),  
 (C08L71/12,25:06)**

30 Priority: 31.08.88 JP 215095/88  
 30.09.88 JP 244581/88  
 30.09.88 JP 244583/88  
 43 Date of publication of application:  
 07.03.90 Bulletin 90/10  
 54 Designated Contracting States:  
**AT BE CH DE ES FR GB IT LI NL SE**

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54 **Styrene-based polymer composition, stretched molding thereof and process for producing the same.**

57 There is disclosed a styrene-based polymer composition which comprises  
 (A) 10 to 98% by weight of a styrene-based polymer having syndiotactic configuration with a racemic pentad of 30% or more and  
 (B) 90 to 2% by weight of polyphenylene ether having an intrinsic viscosity of 0.28 dl/g or more at 30 °C in chloroform.  
 Also, a flame retarder, a flame-retardant aid, a rubber-like elastomer or an inorganic filler may optionally be added to the composition.  
 Further, also disclosed is a stretched molding comprising stretching the above composition.

**EP 0 356 857 A2**

**STYRENE-BASED POLYMER COMPOSITION, STRETCHED MOLDING THEREOF AND PROCESS FOR PRODUCING THE SAME****BACKGROUND OF THE INVENTION**

## 5 1. Field of the Invention

This invention relates to a styrene-based polymer composition, a stretched molding thereof and a process for producing the same. More specifically, it relates to a styrene-based polymer composition which is suitable for materials such as the exterior trim parts of an automobile, engine compartment parts,  
10 machine parts, electric and electronic parts, domestic kitchenware, etc. a stretched molding thereof and a process for efficiently producing the stretched molding.

## 15 2. Description of the Related Arts

Heretofore, a composition which comprises a polyphenylene ether resin (polyphenylene oxide) (hereinafter referred to as "PPE") and a styrene-based polymer has been widely used as engineering plastics which are excellent in mechanical properties and heat resistance. Such compositions have been described in, for example, Japanese Patent Applications Laid-Open No. 5085/1971 and No. 39457/1972,  
20 and U.S. Patent No. 3,383,435.

However, these compositions have serious drawbacks in that solvent resistance, particularly resistance to aromatic hydrocarbon type solvents, is little, whereby their uses are limited. This can be considered as an essential drawback belonging to the styrene-based polymer having atactic configuration as one component of the composition.

25 Also, PPE generally has self-extinguishing properties and therefore, a resin composition containing PPE also has flame retardance to some degree. However, demands on flame retardance in electric and electronic fields and automobile fields in recent years has become increasingly severe, so that the above demands cannot be satisfied with the flame retardance due to the self-extinguishing properties which PPE originally has.

30 In general, styrene-based polymers have been prepared by radical polymerization. The styrene-based polymers thus prepared have atactic configuration in stereoregularity. However, in such styrene-based polymers, improvement in physical properties by stretching cannot be expected. Also, styrene-based polymers having isotactic configuration in stereoregularity have also been known and an attempt to stretch the polymer has been made (Polymer Chemistry, vol., 21, p. 206 (1964)). However, the styrene-based  
35 polymers have slow crystallization rate and its crystalline structure is helical so that sufficient stretching effect cannot be essentially obtained.

The group of the present inventors' has proposed a process for producing a film-like molding by stretching a styrene-based polymer having mainly syndiotactic configuration and a resin composition comprising the above styrene-based polymer and other thermoplastic resins and/or rubber in Japanese  
40 Patent Applications No. 3847/1988, No. 4921/1988, No. 4923/1988 and No. 4924/1988. In these applications, a low molecular weight PPE having a molecular weight of 10,000 or less is disclosed as one example of the thermoplastic resin.

However, after further investigation concerning the composition, it has found that there is room for further improvement since mechanical properties, solvent resistance and flame retardance are insufficient  
45 due to low molecular weight of PPE.

Also, as proposed in the above Japanese Patent Application No. 3847/1988, the above styrene-based polymer becomes a stretched molding having excellent transparency and high modulus of elasticity by stretching. However, this stretched molding has a disadvantage in that its mechanical strength is low, as compared with stretched polyester film or polyamide film. Therefore, in order to improve its mechanical  
50 strength, an attempt of blending the aforesaid styrene-based polymer having syndiotactic configuration with other resins (particularly a low molecular weight PPE) has been made (Japanese Patent Application No. 4921/1988).

However, according to research thereafter, it has been found that this blended material is still insufficient in mechanical strength of its stretched molding due to the low molecular weight of PPE.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a styrene-based polymer composition which can produce a molding improved in mechanical properties and solvent resistance.

Also, another object of the present invention is to provide a styrene-based polymer composition which is excellent in the above mechanical properties and solvent resistance as well as flame retardance.

Further, other object of the present invention is to provide a stretched molding which is excellent in mechanical properties and solvent properties while maintaining transparency, high elasticity and electric characteristics which the styrene-based polymer has originally.

Moreover, a still further object of the present invention is to provide a process for producing the above stretched molding with good efficiency.

The present invention is to provide a styrene-based polymer composition which comprises (A) 10 to 98% by weight of a styrene-based polymer having syndiotactic configuration with a racemic pentad of 30% or more and (B) 90 to 2% by weight of PPE having an intrinsic viscosity of 0.28 dl/g or more at 30°C in chloroform.

Also, the present invention is to provide a stretched molding prepared by stretching the above resin composition.

Further, the present invention is to provide a process for producing a stretched molding, which comprises heat melting the above composition, quenching the molten composition to a temperature lower than a glass transition temperature of the composition to form a sheet, and then subjecting the sheet to stretching treatment with heating to a temperature between the glass transition temperature and a melting point of the composition.

DESCRIPTION OF PREFERRED EMBODIMENTS

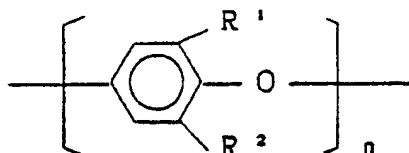
The styrene-based polymer composition of the present invention comprises the above components (A) and (B) as main components. Here, the component (A) is a styrene-based polymer having syndiotactic configuration with a racemic pentad of 30% or more, and the syndiotactic configuration means that a stereostructure is mainly syndiotactic, i.e., the stereostructure in which phenyl groups or substituted phenyl groups as side chains are located alternately at opposite directions relative to the main chain consisting of carbon-carbon bonds. The tacticity is quantitatively determined by the nuclear magnetic resonance method using carbon isotope (<sup>13</sup>C-NMR) method. The tacticity as determined by the <sup>13</sup>C-NMR method can be indicated in terms of proportions of structural units continuously connected to each other, i.e., a diad in which two structural units are connected to each other, a triad in which three structural units are connected to each other, or pentad in which five structural units are connected to each other. Styrene-based polymers having the syndiotactic configuration of the present invention include polystyrene, poly(alkylstyrene), poly(halogenated styrene), poly(alkoxystyrene), poly(vinyl benzoate) and the mixtures thereof, and copolymers containing the above polymers as one of the components, having such a syndiotacticity that the proportion of racemic pentad is 30% or more, preferably 50% or more. The poly(alkylstyrene) can include poly(methylstyrene), poly(ethylstyrene), poly(isopropylstyrene), poly(tert-butylstyrene), poly(divinyl benzene), etc.; the poly(halogenated styrene) can include poly(chlorostyrene), poly(bromostyrene), poly(fluorostyrene), etc. Also, the poly(alkoxystyrene) can include poly(methoxystyrene), poly(ethoxystyrene), etc. Among these, particularly preferred styrene-based polymers include polystyrene, poly(p-methylstyrene), poly(m-methylstyrene), poly(p-tert-butylstyrene), poly(p-chlorostyrene), poly(m-chlorostyrene), poly(p-fluorostyrene), poly(divinyl benzene), and further a copolymer comprising at least one of the above polymers as partial component (Japanese Patent Application Laid-Open No. 187708/1987).

The molecular weight of the styrene-based polymer to be used in the present invention is not specifically limited, but the styrene-based polymer having a weight average molecular weight of 10,000 or more is preferred, and particularly that of 50,000 to 1,000,000 is optimum. If the weight average molecular weight is less than 10,000, mechanical properties are inferior and there is a tendency of lacking solvent resistance. Further, the molecular weight distribution thereof is also not limited, and the styrene-based polymer having various ranges can be used. Such a styrene-based polymer having syndiotactic configuration, has a melting point of 160 to 310°C and is extremely excellent in heat resistance, as compared with the conventional styrene-based polymer having atactic configuration.

Such a styrene-based polymer having syndiotactic configuration can be prepared by, for example, polymerizing a styrene-based monomer (a monomer corresponding to the above styrene-based polymer) using a titanium compound and a condensate product of water and trialkylaluminum as catalysts in an inert

hydrocarbon solvent or in the absence of a solvent (see U.S. Patent No. 4,680,353).

On the other hand, the component (B) to be used in the present invention is represented by the following formula:



wherein R<sup>1</sup> and R<sup>2</sup> may be the same or different and each represent an alkyl group having 1 to 6 carbon atoms, an aryl group having 6 to 8 carbon atoms, a halogen atom or a hydrogen atom, and n is an integer of 50 to 500, preferably 100 to 450.

Specific examples of such polyphenylene ether resins include poly(2,6-dimethyl-1,4-phenylene)ether; poly(2,6-diethyl-1,4-phenylene)ether; poly(2-methyl-6-ethyl-1,4-phenylene)ether; poly(2-methyl-6-isopropyl-1,4-phenylene)ether; poly(2-methyl-1,4-phenylene)ether; poly(2,6-dichloro-1,4-phenylene)ether; poly(2-ethyl-6-bromo-1,4-phenylene)ether; poly(2-phenyl-1,4-phenylene)ether, etc. Among these, poly(2,6-dimethyl-1,4-phenylene)ether is particularly suitable. PPE to be used in the present invention is required to have an intrinsic viscosity in chloroform at 30 °C of 0.28 dl/g or more, and preferably 0.3 to 0.66 dl/g. If the intrinsic viscosity is less than 0.28 dl/g, mechanical properties and solvent resistance become insufficient.

The composition of the present invention comprises the above component (A) and component (B) as main components, and the blending ratio of both components is 10 to 98% by weight, preferably 20 to 95% by weight, more preferably 30 to 95% by weight of the component (A) and 90 to 2% by weight, preferably 80 to 5% by weight, more preferably 70 to 5% by weight of the component (B). If the component (A) is less than 10 % by weight, solvent resistance is low and if it exceeds 98% by weight, elongation (toughness) is low. Also, if the component (B) exceeds 90% by weight, solvent resistance is low and thermal degradation of PPE becomes remarkable so that molding becomes difficult, and if it is less than 2% by weight, elongation is low.

The composition of the present invention basically comprises the above components (A) and (B), but if necessary, its flame retardance can be improved by adding a flame retarder as a component (C) and a flame-retardant aid as a component (D).

As the above flame retarder, various ones may be mentioned, but halogen-based flame retarders and phosphorus-based flame retarders are particularly preferred. The halogen-based flame retarders include, for example, tetrabromobisphenol A, tetrabromophthalic anhydride, hexabromobenzene, tribromophenylallyl ether, pentabromotoluene, pentabromophenol, tribromophenyl-2,3-dibromo propyl ether, tris(2,3-dibromopropyl)phosphate, tris(2-chloro-3-bromopropyl)phosphate, octabromodiphenyl ether, decabromodiphenyl ether, octabromodiphenyl, pentachloropentacyclodecane, hexabromocyclododecane, hexachlorobenzene, pentachlorotoluene, hexabromobiphenyl, decabromobiphenyl, decabromobiphenyl oxide, tetrabromobutane, decabromodiphenyl ether, hexabromodiphenyl ether, ethylene-bis-(tetrabromophthalimide), tetrachlorobisphenol A, tetrabromobisphenol A, oligomer of tetrachlorobisphenol A or tetrabromobisphenol A, halogenated polycarbonate oligomer such as brominated polycarbonate oligomer, halogenated epoxy compound, polychlorostyrene, brominated polystyrene such as poly(tribromostyrene), poly(dibromophenylene oxide), bis(tribromophenoxy)ethane, etc.

On the other hand, the phosphorus-based flame retarders include, for example, ammonium phosphate, tricresyl phosphate, triethyl phosphate, acidic phosphate, triphenylphosphine oxide, etc.

As the flame retarders among these, poly (tribromostyrene), poly(dibromophenylene oxide) and decabromodiphenyl ether are particularly preferred.

The above component (C) (flame retarder) is blended at a ratio of 3 to 40 parts by weight, preferably 5 to 35 parts by weight, more preferably 10 to 35 parts by weight based on 100 parts by weight of the components (A) and (B) (total amount).

If the blending ratio of the component (C) is less than 3 parts by weight, flame retardance of the resulting composition is insufficient.

On the other hand, if it is added in excess of 40 parts by weight, flame retardance is not improved according to the ratio added, but rather the mechanical properties and solvent resistance are undesirably lowered.

As the flame-retardant aids, various ones may be mentioned, and they include, for example, antimony flame-retardant aids such as antimony trioxide, antimony pentoxide, sodium antimonate, metal antimony,

antimony trichloride, antimony pentachloride, antimony trisulfide, antimony pentasulfide, etc. Also, in addition to the above, there may be mentioned zinc borate, barium metaborate, zirconium oxide, etc.

Among these, as the component (D), antimony trioxide is particularly preferred.

The component (D) (flame-retardant aid) is blended with a ratio of 1 to 15 parts by weight, preferably 2 to 10 parts by weight based on 100 parts by weight of the components (A) and (B) (total amount).

If the blending ratio of the component (D) is less than 1 part by weight, the effects due to the flame-retardant aid are insufficient. On the other hand, if it exceeds 15 parts by weights, effects due to a flame-retardant aid are not improved according to the ratio added, but rather there exists the possibility of impairing other properties so that it is not preferred.

These components (C) and (D) are preferably blended in combination and when both components are used, a remarkably increased flame-retardant effect can be developed than in the case where only either one of the components (C) or (D) is used. Even small amounts of flame retarder and flame-retardant aid result in the increased flame-retardant effect since the component (B) is added.

Further, in the composition of the present invention, if necessary, a rubber-like elastomer and/or an inorganic filler may be blended as a component (E). These rubber-like elastomer and/or inorganic filler are blended in the above components (A) and (B) simultaneously with the above components (C) and (D), or separately from the components (C) and (D) so that mechanical properties, particularly impact resistance, etc. of the composition are further improved.

The rubber-like elastomer to be used as the component (E) may be various ones, but particularly suitable ones are a rubber-like copolymer containing a styrene-based compound as one component. There may be mentioned, for example, styrene-butadiene copolymer rubber (SBR), a rubber in which a part or all of the butadiene portion of a styrene-butadiene block copolymer is hydrogenated (SEBS), a styrene-isoprene copolymer rubber, a rubber in which a part or all of the isoprene portion of a styrene-isoprene block copolymer is hydrogenated, or as described in Japanese Patent Application No. 127100/1988, a granular elastomer obtained by polymerizing a vinyl-based monomer in the presence of the polymer obtained by polymerizing at least one monomer selected from the group consisting of an alkylacrylate, an alkylmetal methacrylate and a polyfunctional monomer having a conjugated diene type double bond, such as acrylonitrile-styrene grafted butadiene rubber (ABS), acrylonitrile-styrene grafted butadiene-butyl acrylate copolymer rubber (AABS), methyl methacrylate-styrene grafted butylacrylate rubber (MAS), styrene grafted butadiene rubber (SB), methyl methacrylate-styrene grafted butadiene rubber (MBS), methyl methacrylate-styrene grafted butadiene-butyl acrylate copolymer rubber (MABS), etc. Since these materials each have styrene structure, dispersibility in the above styrene-based polymer having syndiotactic configuration is good and as a result, improved effects in physical property is remarkable.

Further, examples of the rubber-like elastomer include, in addition to the above, natural rubber, polybutadiene, polyisoprene, polyisobutylene, neoprene, ethylene-propylene copolymer rubber, polysulfide rubber, thiokol rubber, acrylic rubber, urethane rubber, silicone rubber, epichlorohydrin.

The above rubber-like elastomer is blended in the ratio of 5 to 85 parts by weight, preferably 10 to 50 parts by weight based on 100 parts by weight of the components (A) and (B) (total amount). Mechanical properties, particularly impact resistance, are further improved by blending the rubber-like elastomer. If the blending ratio is less than 5% by weight, improvements in impact resistance or stretch are insufficient, while if it exceeds 85 parts by weight, improvement in heat resistance and solvent resistance are low.

As for the inorganic filler which can be used in place of the above rubber-like elastomer, or with the rubber-like elastomer as the component (E) in the present invention, it may be in the form of fiber, particles or powders. The fibrous inorganic filler includes glass fiber, carbon fiber, alumina fiber, etc., and glass fiber and carbon fiber are particularly preferred. As the shape of the glass fiber, there can be mentioned cross state, mat state, bundling cut state, short fiber, filament state, etc., but preferably the bundling cut state having a length of 0.05 mm to 13 mm and a diameter of the fiber of 5 to 20  $\mu\text{m}$ , and particularly preferred are those which are treated with a silane series agent. Also, the carbon fibers preferably include polyacrylonitrile (PAN)-based ones, more preferably bundled materials of chopped fiber type having a length of 3 mm or so and a diameter of 7 to 15  $\mu\text{m}$ .

On the other hand, as the particle and powder inorganic fillers, there can be mentioned talc, carbon black, graphite, titanium dioxide, silica, mica, calcium carbonate, calcium sulfate, barium carbonate, magnesium carbonate, magnesium sulfate, barium sulfate, oxysulfate, tin oxide, alumina, kaolin, silicon carbide, metal powder, etc., and talc, calcium carbonate and mica are particularly preferred. A preferred average particle size of talc is 0.3 to 20  $\mu\text{m}$ , more preferably 0.6 to 10  $\mu\text{m}$ . A preferred average particle size of calcium carbonate is 0.1 to 20  $\mu\text{m}$ . A preferred average particle size of mica is 40 to 250  $\mu\text{m}$ , more preferably 50 to 150  $\mu\text{m}$ .

The above inorganic filler is blended in a ratio of 1 to 250 parts by weight, preferably 10 to 150 parts by

weight based on 100 parts by weight of the above components (A) and (B) (total amount). If the blended ratio of the inorganic filler is less than 1 part by weight, sufficient effects due to the filler cannot be observed. On the other hand, if it exceeds 250 parts by weight, the filler cannot be dispersed uniformly and resulting composition becomes inferior in mechanical strength.

5 In the composition which comprises blending simultaneously the components (A) to (E), the component (C) is blended in a ratio of 3 to 40 parts by weight, preferably 5 to 35 parts by weight based on 100 parts by weight of the components (A) and (B) (total amount).

The reason why the blending ratio is specified is the same as described in the explanation concerning the composition comprising the above components (A) to (D).

10 Regarding the component (D), it is blended in the ratio of 1 to 15 parts by weight, preferably 2 to 10 parts by weight based on 100 parts by weight of the components (A) and (B) (total amount) as in the above. The reason why the blending ratio is specified is also as the same described in the explanation concerning the composition comprising the above components (A) to (D).

The composition of the present invention are prepared by blending the above components (A) and (B),  
15 and if necessary, further blending the components (C) to (E). Various additives or other synthetic resins may further be blended, otherwise inhibiting the object of the present invention. As the aforesaid additive, there can be mentioned, for example, antioxidants such as phosphites and phosphates; UV absorbers such as benzotriazoles and benzophenones; external lubricants such as aliphatic carboxylates and paraffins; nuclear agents used conventionally, releasing agents, antistatic agents, coloring agents, etc. As the other  
20 synthetic resins, there can be mentioned resins such as polyethylene, polypropylene, polystyrene, AS resin, ABS resin, polymethylmethacrylate, etc.

The composition of the present invention can be obtained by blending the above components (A) and (B), and if necessary, the components (C) to (E), and further various desired components, and then kneading at an optional temperature, for example, between a melting point and a temperature 80°C higher  
25 than the melting point. The blending and kneading procedures at this time can be carried out according to the conventional method. More specifically, the fusion-kneading method by using a kneader, a mixing roll, a uniaxial (monoaxial) or biaxial extruder, Banbury mixer, Henschel mixer or a kneading roll, or the solution blending method, etc. These compositions are molded into a tridimensional molding by the general method, preferably by an injection molding machine.

30 Also, in the molding and the process for producing the same of the present invention, a raw molding material is prepared by blending the above components (A) and (B), and further, if necessary, blending other components in optional amounts. The raw material is generally molded by an extrusion molding, a calendar molding, or further subjected to injection molding in case of a blow molding or a blow stretch molding to form a preform for stretching (sheet, plate, film, tube, bottle, etc.). In this molding, the above raw  
35 material for molding is usually melted by heating and molded in the desired form by use of various molding machines, but the raw material for molding may be molded in a softened state without heat melting. The melting temperature of the raw material for molding is generally from its melting point to a temperature 80°C higher than its melting point. If the temperature is too high, undesirable problems occur, such as decomposition of the raw material for molding. Also, the thickness of the preform to be molded is not  
40 limited and is optionally selected, but generally it is usually chosen from the range of 5 mm or less, preferably 3 mm to 10 μm. If the thickness exceeds 5 mm, tension at stretching is large so that the stretching may sometimes become difficult. The crystallinity of the preliminary molding is 30% or lower, preferably 25% or lower.

In the process for producing the molding of the present invention, the above raw material for molding  
45 which has been heat melted is cooled at the time of molding for producing a preform having preferred crystallinity. Cooling should be carried out at a temperature lower than a temperature 30°C above, preferably 20°C above, the glass transition temperature of the composition. The cooling rate is 50 to 3°C/sec, preferably 50 to 5°C/sec.

In the process of the present invention, the preform thus obtained is heated to a temperature capable of  
50 effecting stretching. The temperature at this time should be set in the range between the glass transition temperature and the melting point of said composition.

Further, according to the process of the present invention, the preform heated to the temperature suitable for stretching is stretched uniaxially or biaxially. In the case of uniaxially stretching, the preform should be stretched at a draw ratio of at least 1.5-fold. If the draw ratio is less than 1.5-fold, strength and  
55 heat resistance become insufficient. Also, in the case of biaxially stretching, the preform should be stretched at a draw ratio of at least 1.2-fold to the respective stretching direction (biaxial direction). If the draw ratio is too small, strength and heat resistance of the resulting stretched molding become insufficient. In the above biaxially stretching, the preform may be stretched simultaneously in the machine direction

(MD) and transverse direction (TD), or may be stretched sequentially in the desired order. As the means for stretching, there may be employed the means of tenter, milling, calendering, stretching between rolls, stretching due to gas pressure, etc.

In the process of the present invention, particularly in the case of biaxially stretching, the above raw material for molding can be directly subjected to inflation molding at the temperature of not more than its melting point without formation of a preform after heat melting to produce a biaxially stretched molding (e.g., a biaxially stretched film, etc.). In this inflation molding, it is effective so as to prevent melt fracture, roughness of surface and the like that the composition be maintained at a temperature of at least 20 °C higher than its melting point. If, however, the melt temperature is too high, degradation of the composition becomes remarkable so that it is preferred to set the temperature within the range of the melting point to a temperature 80 °C higher than the melting point. Further, the stretching temperature is preferably 5 to 150 °C lower than the melting point and more preferably 10 to 50 °C lower than the same. Also, if the blow-up ratio is decreased, uniaxially stretching is realized in inflation.

When the uniaxially stretching or biaxially stretching is carried out according to the process of the present invention, a stretched molding (sheet, plate, film, tube, bottle, etc.) having excellent heat resistance, solvent resistance and electric insulating properties can be obtained. Also, when dimensional stability at high temperature, and heat resistance is required, it is preferred to further carry out annealing. The annealing can be carried out by the conventional method, but the stretched molding is subjected to annealing under tension at a temperature ranging from 100 °C, preferably a temperature higher than the glass transition temperature of said composition, to the melting point. By annealing at temperatures lower than glass transition temperature, thermal properties of the stretched molding cannot be improved, while at the temperature more than the melting point, the stretched molding is fused. The annealing is usually carried out for 0.5 seconds to 100 hours, preferably 0.5 seconds to 10 hours, further preferably 0.5 to 300 seconds. This annealing further increases heat resistance, dimensional stability, etc. of the stretched molding.

As described above, the styrene-based polymer composition comprising the styrene-based polymer and the polyphenylene ether resin of the present invention is remarkable excellent in solvent resistance. Further, the composition blended with the rubber-like elastomer is well balanced in mechanical properties, heat resistance, solvent resistance, etc.

Also, the resin composition of the present invention in which the flame retarder or the flame-retardant aid is further added, has sufficient flame retardance and also excellent mechanical properties, solvent resistance, etc.

Further, the stretched molding of the composition of the present invention has excellent mechanical strength and elongation while maintaining transparency, high modulus of elasticity and electric properties.

Accordingly, the composition of the present invention can be utilized for various fields including automobile parts such as exterior trim parts of an automobile, engine compartment parts, etc., as engineering plastics, and further for various machine parts, electric and electronic parts, domestic kitchen-ware, etc. Also, the stretched molding of the present invention can be expected to be effectively used such as a film for electric field, e.g., a film for a flexible print substrate, an encapsulation film, etc., and a general film for industrial use such as magnetic tape, hot stamping, decoration and others.

The present invention is described in greater detail with reference to the following examples.

#### REFERENCE EXAMPLE 1 (Production of Polystyrene having Syndiotactic Configuration)

Two liters of toluene as a solvent, and 5 mmol of tetraethoxytitanium and 500 mmol (as aluminum atom) of methylaluminoxane as catalyst components were placed in a reactor, and 15 L (L = liter) of styrene was added thereto at 55 °C and polymerized for 4 hours.

After polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose the catalyst components, and then dried to obtain 2.5 kg of a styrene-based polymer (polystyrene). The polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 97% by weight of an extraction residue. Said residue had a weight average molecular weight of 400,000, a number average molecular weight of 180,000, and a melting point of 269 °C. A nuclear magnetic resonance analysis using carbon isotope (<sup>13</sup>C-NMR Analysis, Solvent: 1,2-dichlorobenzene) of the polymer showed an absorption at 145.35 ppm, ascribable to the syndiotactic configuration. The syndiotacticity in terms of racemic pentad as calculated from the peak area was 98%.

REFERENCE EXAMPLE 2

Poly(2,6-dimethyl-1,4-phenylene)ether powder was obtained from GEM Polymer CO., Ltd. Intrinsic viscosity of this powder in chloroform at 30 °C was 0.49 dl/g.

EXAMPLE 1

Zero point seven part by weight of (2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite (Trade Name: PEP-36, produced by Adeka Argus Co., Ltd.) and 0.1 part by weight of 2,6-di-tert-butyl-4-methylphenol (Trade Name: Sumilizer BHT, produced by Sumitomo Chemical Co., Ltd.) were added as antioxidants to 100 parts by weight of a resin mixture consisting of 50% by weight syndiotactic polystyrene (SPS) obtained in Reference Example 1 and 50% by weight poly(2,6-dimethyl-1,4-phenylene)ether described Reference Example 2, and kneaded with a uniaxial kneading extruder, to be pelletized.

The resulting pellet was injection-molded into three kinds of test pieces, that is, test pieces for Izod impact strength test in accordance with JIS K-7110, tensile strength test in accordance with JIS K-7113 and bending test in accordance with JIS K-7203.

The piece bending test was dipped in a regular gasoline (Trade Name: Idemitsu Red Apollo, produced by Idemitsu Kosan Co., Ltd.) and left for 24 hours at room temperature. After that, its appearance and the ratio of weight change as defined below was evaluated. The results are shown in Table 1. The same dipping test was performed also with acetone, carbon tetrachloride, ethyl acetate and n-pentane. The results are shown in Table 1.

the ratio of weight change =  $(W.A.D.^{*1} - W.B.D.) / W.B.D.^{*2}$

Further, the bending test piece was measured for bending strength, and the tensile strength test piece was measured for elongation. The results are shown in Table 2.

EXAMPLE 2

The procedure of Example 1 was repeated except that the proportion of SPS obtained Reference Example 1 and poly(2,6-dimethyl-1,4-phenylene)ether described in Reference Example 2 was 75%/25% by weight, to form test pieces. The results of dipping test are shown in Table 1, and the results of measurement in bending strength and elongation are shown in Table 2.

EXAMPLE 3

The procedure of Example 1 was repeated except that 12.5 parts by weight of styrenegrafted butadiene rubber (particle diameter: 0.7 μm, Trade Name: Metablen IP-2, produced by Mitsubishi Rayon Co., Ltd.) as rubber-like elastomer was added to 100 parts by weight of the resin mixture, to form test pieces. The results of dipping test are shown in Table 1. Further, tensile strength test, bending test and notched Izod impact test were conducted. The results are shown in Table 3.

EXAMPLE 4

The procedure of Example 2 was repeated except that 18.75 parts by weight of styrenegrafted butadiene rubber (particle diameter: 0.7 μm, Trade Name: Metablen IP-2, produced by Mitsubishi Rayon Co., Ltd.) as rubber-like elastomer was added to 100 parts by weight of the resin mixture, to form test pieces. The results of dipping test are shown in Table 1. Further, tensile test, bending test and notched Izod impact test were conducted, and the results are shown in Table 3.

\*1 W.A.D. : weight after dipping

\*2 W.B.D. : weight before dipping

EXAMPLE 5

The procedure of Example 1 was repeated except that 60 parts by weight of MAS rubber (Trade Name: KM-330, produced by Rohm & Haas Company) as rubber-like elastomer was added to 100 parts by weight of the resin mixture consisting of 90% by weight SPS obtained in Reference Example 1 and 10% by weight poly(2,6-dimethyl-1,4-phenylene)ether described in Reference Example 2, to form test pieces. The results of dipping test conducted on the said test pieces are shown in Table 1.

10 EXAMPLE 6

The procedure of Example 1 was repeated except that 35 parts by weight of SBS rubber (Trade Name: TR-1184, produced by Shell Chemical Co., Ltd.) as rubber-like elastomer was added to 100 parts by weight of the resin mixture consisting of 30% by weight SPS obtained in Reference Example 1 and 70% by weight poly(2,6-dimethyl-1,4-phenylene)ether described in Reference Example 2, to form test pieces. The results of dipping test conducted on the said test pieces are shown in Table 1.

20 EXAMPLE 7

Zero point seven part by weight of (2,6-tert-butyl-4-methylphenylene)pentaerythritol diphosphite (Trade Name: PEP-36, produced by Adeka Argus Chemicals Co., Ltd.) and 0.1 part by weight of 2,6-di-tert-butyl-4-methylphenol (Trade Name: Sumilizer, produced by Sumitomo Chemical Co., Ltd.) were added to 100 parts by weight of a resin mixture consisting of 90% weight SPS obtained in Reference Example 1 and 10% by weight poly(2,6-dimethyl-1,4-phenylene)ether described in Reference Example 2, and 43 parts by weight of glass fiber were mixed thereto further, and dry-blended. Then the blend was kneaded with the use of a twin screw kneading extruder, and pelletized.

The resulting pellet was made into three kinds of test pieces, that is, test pieces for Izod impact strength test bending test.

30 The result of bending test and Izod impact test using thus obtained test piece is shown in Table 3.

EXAMPLES 8 and 9

35 The procedure of Example 7 was repeated except that the substances shown in Table 3 were compounded in prescribed ratios as components (A) to (E), to obtain various test pieces, which were evaluated for physical properties in the same manner as in Example 7. The results are shown in Table 3.

40 COMPARATIVE EXAMPLE 1

The procedure of Example 1 was repeated except that a styrene polymer resin having atactic configuration (Trade Name: Idemitsu Polystyrene US-305, produced by Idemitsu petrochemical Co., Ltd.) as styrene-based polymer resin was used in place of syndiotactic polystyrene, to form test pieces. The results of dipping test are shown in Table 1.

COMPARATIVE EXAMPLE 2

50 The procedure of Example 2 was repeated except that Polystyrene US-305 was used as styrene-based resin in place of syndiotactic polystyrene, to form test pieces. The results of dipping test are shown in Table 1.

55 COMPARATIVE EXAMPLE 3

The procedure of Example 3 was repeated except that Polystyrene US-305 was used as styrene based resin in place of syndiotactic polystyrene, to form test pieces. The results of dipping test are shown in

Table 1.

COMPARATIVE EXAMPLE 4

The procedure of Example 4 was repeated except that Polystyrene US-305 was used as styrene-based resin in place of syndiotactic polystyrene, to form test pieces. The results of dipping test are shown in Table 1.

COMPARATIVE EXAMPLE 5

The procedure of Example 5 was repeated except that Polystyrene US-305 was used as styrene-based resin in place of syndiotactic polystyrene, to form test pieces. The results of dipping test are shown in Table 1.

COMPARATIVE EXAMPLE 6

The procedure of Example 6 was repeated except that Polystyrene US-305 was used as styrene-based resin in place of syndiotactic polystyrene, to form test pieces. The results of dipping test are shown in Table 1.

COMPARATIVE EXAMPLE 7

The procedure of Example 1 was repeated except that the proportion of syndiotactic polystyrene obtained in Reference Example 1 and poly(2,6-dimethyl-1,4-phenylene)ether described in Reference Example 2 was 2%/98% by weight, to form test pieces. The results of dipping test are shown in Table 1.

COMPARATIVE EXAMPLE 8

The procedure of Example 1 was repeated except that poly(2,6-dimethyl-1,4-phenylene)ether described in Reference Example 2 was not used, but that an antioxidant having the same prescription as in Example 1 was added to 100 parts by weight of syndiotactic polystyrene obtained in Reference Example 1, to form test pieces. The results of measurement for bending strength and elongation are shown in Table 2.

COMPARATIVE EXAMPLE 9

The procedure of Example 2 was repeated except that a polyphenylene ether resin having a weight average molecular weight of 7200, and an intrinsic viscosity of 0.24 dl/g (produced by Scientific Polymer Products Incorporated, Catalogue No. V-100) was used as polyphenylene ether resin, to form test pieces. The results of measurement for bending strength and elongation are shown in Table 2.

COMPARATIVE EXAMPLE 10

The procedure of Example 1 was repeated except that 25 parts by weight of styrene-grafted butadiene rubber (Trade Name: Mitsubishi Metablen IP-2, produced by Mitsubishi Rayon Co., Ltd.) to 100 parts by weight of SPS obtained in Reference Example 1, but that polyphenylene ether resin was not added. The test pieces thus obtained were subjected to tensile strength test, bending test, and notched Izod impact test, of which results are shown in Table 3.

COMPARATIVE EXAMPLE 11

The procedure of Example 1 was repeated except that 100 parts by weight of SBS rubber (Trade Name: TR-1184, produced by Shell Chemical Co., Ltd.) was added to 100 parts by weight of a resin mixture consisting of 50% by weight SPS obtained in Reference Example 1 and 50% by weight poly (2,6-dimethyl-1,4-phenylene)ether described in Reference Example 2, but the resulting mixture was too soft at injection molding to release.

#### EXAMPLE 10

Zero point seven part by weight of (2,6-di-tert-butyl-4-methylphenylene)pentaerythritol diphosphite (Trade Name: PEP-36, produced by Adeka Argus Chemicals Co., Ltd.) and 0.1 part by weight of 2,6-di-tert-butyl-4-methylphenol (Trade Name: Sumilizer, produced by Sumitomo Chemical Co., Ltd.) were added to 100 parts by weight of a resin mixture consisting of 50% by weight SPS obtained in Reference Example 1 and 50% by weight poly(2,6-dimethyl-1,4-phenylene)ether described in Reference Example 2, and 12 parts by weight of polytribromostyrene and 3 parts by weight of antimony trioxide ( $\text{Sb}_2\text{O}_3$ ) were mixed thereto further, and dry-blended. Then the blend was kneaded with the use of a twin screw kneading extruder, and pelletized.

The resulting pellet was made into three kinds of test pieces, that is, test pieces for tensile strength test, bending test, and flame retardance test in accordance with UL-94.

The result of flame retardance test using thus obtained test piece is shown in Table 4.

The results of dipping the bending test pieces in a regular gasoline similar to that of Example 1 are shown in Table 5. Moreover, elongation of tensile strength test piece were measured, respectively. The results are shown in Table 5.

#### EXAMPLES 11 to 18 and COMPARATIVE EXAMPLES 12 and 13

The procedure of Example 10 was repeated except that the substances shown in Table 4 were compounded in prescribed ratios as components (A) to (E), to obtain various test pieces, which were evaluated for physical properties in the same manner as in Example 10. The results are shown in Tables 4 and 5.

#### REFERENCE EXAMPLE 3 (Production of Polystyrene having Syndiotactic Configuration)

Two liters of toluene as a solvent, and 1 mmol of cyclopentadienyltitanium trichloride and 0.8 mol (as aluminum atom) of methylaluminoxane as catalyst components were placed in a reactor, and 3.6 L of styrene was added at 20°C and polymerized for 1 hour.

After the polymerization, the reaction product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components, and then dried to obtain 330 g of a styrene-based polymer (polystyrene).

Said polymer was subjected to Soxhlet extraction using methyl ethyl ketone as a solvent to obtain 95% by weight of an extraction residue. The polymer had a weight average molecular weight of 290,000, a number average molecular weight of 158,000 and a melting point of 270°C. A  $^{13}\text{C}$ -NMR analysis showed an absorption at 145.35 ppm, ascribable to the syndiotactic configuration, and the syndiotacticity in terms of pentad as calculated from the peak area was 96%.

#### EXAMPLE 19

Poly(2,6-dimethyl-1,4-phenylene)ether having an intrinsic viscosity of 0.32 dl/g was blended to the syndiotactic polystyrene (SPS) obtained in Reference Example 3 in the proportion of 5%/95% by weight, wherein 0.7 part by weight of (2,6-di-tert-butyl-4-methylphenyl)pentaerythritol diphosphite (Trade Name: PEP-36, produced by Adeka Argus Chemical Co., Ltd.) and 0.1 part by weight of tetrakis (methylene(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate) methane (Trade Name: Irganox 1010, produced by Ciba Geigy Corporation, Japan) were added. The glass transition temperature of the resulting composition was 96°C.

Subsequently, resulting composition was melted at 300°C to be press-molded, and then cooled to 25°C in 30 seconds, to obtain a transparent sheet with the thickness of 300 μm. The sheet thus obtained

was preheated at 120 °C in a table tenter for 5 minutes, to be uniaxially stretched at a draw ratio of four. The physical properties of the resulting film are shown in Table 6.

#### 5 EXAMPLE 20

The procedure of Example 19 was repeated except that the sheet obtained in Example 19 was uniaxially stretched at a draw ratio of two. Physical properties of the resulting film are shown in Table 6.

#### 10 EXAMPLE 21

The stretched film obtained in Example 19 was heat-treated under tension at 250 °C for 30 seconds. Physical properties of the resulting film are shown in Table 6.

15

#### COMPARATIVE EXAMPLE 14

20 The procedure of Example 19 was repeated except that the proportion of SPS was 99% by weight and that of PPE was 1% by weight, to prepare a composition. Said composition was melted to mold at 300 °C, and then quenched to 25 °C, to obtain a transparent sheet with a thickness of 300 µm. The sheet thus obtained was preheated in a table tenter at 120 °C for 5 minutes, and then uniaxially stretched at a draw ratio of four. Physical properties of the stretched film are shown in Table 6.

25

#### EXAMPLE 22

The procedure of Example 19 was repeated except that the proportion of SPS and PPE was 80%/20% by weight. Physical properties of the resulting film are shown in Table 6.

30

#### EXAMPLE 23

35 The sheet used in Example 22 was preheated in a table tenter at 120 °C for 30 seconds, and biaxially stretched to 3.5 x 3.5 times the original. Physical properties of the stretched film are shown in Table 6.

#### EXAMPLE 24

40 The film obtained in Example 23 was heat-treated (annealed) at 250 °C for 30 seconds under tension. Physical properties of the resulting film are shown in Table 6.

#### REFERENCE EXAMPLE 4 (Production of Polystyrene having Syndiotactic Configuration)

45

Two liters of toluene as reaction solvent, 5 mmol of tetraethoxytitanium and 500 mmol (as aluminum atom) of methylaluminoxane as catalyst components were placed in a reactor, 15 L of styrene was added at 50 °C, and the resulting mixture was polymerized for 4 hours.

50 After completion of the reaction, the product was washed with a mixture of hydrochloric acid and methanol to decompose and remove the catalyst components. Subsequently the residue was dried, to obtain 2.5 kg of styrene-based polymer polystyrene). Then the polymer was subjected to Soxhlet extraction with methyl ethyl ketone as solvent, to obtain an extraction residue in 95% by weight, having a weight average molecular weight of 800,000. A <sup>13</sup>C-NMR analysis (solvent: 1,2-dichlorobenzene) of the polymer showed an absorption at 145.35 ppm, ascribable to syndiotactic configuration, and the syndiotacticity in terms of racemic pentad calculated from the peak area was 96%.

55

#### EXAMPLE 25

SPS obtained in Reference Example 4 and poly(2,6-dimethyl-1,4-phenylene)ether having an intrinsic viscosity of 0.49 dl/g (produced by GEM Polymer Co., Ltd.) were blended in a proportion of 50%/50% by weight, and an antioxidant in the same amount as in Example 19 was added. The resulting composition was melted at 300°C and compression-molded. Subsequently, the molding was cooled with a chill roll having the surface temperature of 25°C, to produce a transparent sheet with a thickness of 300 μm. The resulting sheet was preheated at 170°C in a table tenter for 5 minutes stretched biaxially to 3.5 x 3.5 times the original, to obtain a film. The physical properties of the stretched film are shown in Table 6.

#### 10 EXAMPLE 26

SPS obtained in Reference Example 4 and PPE same as in Example 25 were blended in the proportion of 15%/85% by weight, and an antioxidant in the same amount as in Example 19 was added. Resulting composition was melted at 300°C, compression-molded, and then quenched to 25°C, to obtain a sheet with a thickness of 300 μm. Said sheet was preheated in a table tenter at 190°C for 30 seconds, stretched biaxially to 3.5 x 3.5 times the original, to obtain a film. Physical properties of the film are shown in Table 6.

#### COMPARATIVE EXAMPLE 15

SPS obtained in Reference Example 4 and the same PPE as in Example 25 are blended in the proportion of 5%/95% by weight, and an antioxidant in the same amount as in Example 19 was added. The resulting composition was melted at 300°C, compression-molded, and quenched to 25°C, but the sample stucked so hard to the press board that no sheet was obtained.

Table 1

No	Component A		Component B		Component E	
	Styrene-based Polymer	wt%	PPE resin <sup>1)</sup>	wt%	Rubber-like elastomer	part 2) by weight
Example 1	Syndiotactic	50	Intrinsic viscosity	0.49	50	None
Example 2	Syndiotactic	75	Intrinsic viscosity	0.49	25	None
Example 3	Syndiotactic	50	Intrinsic viscosity	0.49	50	SB 12.5
Example 4	Syndiotactic	75	Intrinsic viscosity	0.49	25	SB 18.75
Example 5	Syndiotactic	90	Intrinsic viscosity	0.49	10	MAS 60
Example 6	Syndiotactic	30	Intrinsic viscosity	0.49	70	SBS 35
Comparative Example 1	Atactic	50	Intrinsic viscosity	0.49	50	None
Comparative Example 2	Atactic	75	Intrinsic viscosity	0.49	25	None
Comparative Example 3	Atactic	50	Intrinsic viscosity	0.49	50	SB 12.5
Comparative Example 4	Atactic	75	Intrinsic viscosity	0.49	25	SB 18.75
Comparative Example 5	Atactic	90	Intrinsic viscosity	0.49	10	MAS 60
Comparative Example 6	Atactic	30	Intrinsic viscosity	0.49	70	SBS 35
Comparative Example 7	Syndiotactic	2	Intrinsic viscosity	0.49	98	None

Table 1 (continued)

No.	Solvent-dipping Test (left for 1 week at room temperature 3)				
	Acetone	Carbon tetrachloride	Gasoline	Ethyl acetate	n-Heptane
Example 1	B	B	A	B	A
Example 2	A	A	A	A	A
Example 3	B	B	A	B	A
Example 4	A	A	A	A	A
Example 5	A	A	A	A	A
Example 6	B	B	B	B	B
Comparative Example 1	D	D	D	D	B
Comparative Example 2	D	D	D	D	B
Comparative Example 3	D	D	D	D	B
Comparative Example 4	D	D	D	D	B
Comparative Example 5	D	D	D	D	B
Comparative Example 6	D	D	C	D	B
Comparative Example 7	C	C	B	C	B

Note: 1) PPE resin = Polyphenylene ether resin  
 2) Parts by weight based on the total amount of Component A and Component B as 100 parts by weight  
 3) A ... No change in appearance  
 B ... Swollen (increase in weight: not more than 10%)  
 C ... Swollen (increase in weight: 10% or more)  
 D ... Dissolved

Table 2

No.	Component A		Component B			Component E		Bending strength (kg * G/cm <sup>2</sup> )	Tensile fracture elongation (%)
	Styrene-based Polymer	wt%	PPE resin			wt%	Rubber-like elastomer		
Example 1	Syndiotactic	50	Intrinsic viscosity	0.49		50	None	1500	5.4
Example 2	Syndiotactic	75	Intrinsic viscosity	0.49		25	None	1300	3.5
Comparative Example 8	Syndiotactic	100	None			-	None	1000	1.3
Comparative Example 9	Syndiotactic	75	Intrinsic viscosity	0.24		25	None	700	1.3

Table 3

No.	Component A		Component B			Component E		Bending strength (kg·G/cm <sup>2</sup> )	Tensile fracture elongation (%)	Izod impact strength (kg·G·cm/cm)
	Styrene-based Polymer	wt%	PPE resin		wt%	Kind	part by weight *			
Example 3	Syndiotactic	50	Intrinsic viscosity	0.49	50	SB	12.5	1100	25	13
Example 4	Syndiotactic	75	Intrinsic viscosity	0.49	25	SB	18.75	940	16	16
Comparative Example 10	Syndiotactic	100	None		-	SB	12.5	800	2.1	7
Comparative Example 11	Syndiotactic	50	Intrinsic viscosity	0.49	50	SBS	100	Immoldable	Immoldable	Immoldable
Example 7	Syndiotactic	90	Intrinsic viscosity	0.49	10	GF**	43	1520	-	5
Example 8	Syndiotactic	30	Intrinsic viscosity	0.49	70	GF	43	1550	-	4
Example 9	Syndiotactic	90	Intrinsic viscosity	0.49	10	GF talc	130 65	1760	-	4

\*Parts by weight based on the total amount of Component A and Component B as 100 parts by weight

\*\*Glass fiber

Table 4

No.	Component A		Component B		Component C		Component D	
	Styrene- based Polymer	wt%	Intrinsic viscosity of PPE resin	wt%	Flame retarder	part by weight	Flame- retardant aid	part by weight
Example 10	Syndiotactic	50	0.49	50	a	12	Sb <sub>2</sub> O <sub>3</sub>	3
Comparative Example 12	Syndiotactic	100	—	—	a	24	Sb <sub>2</sub> O <sub>3</sub>	6
Example 11	Syndiotactic	75	0.49	25	b	15	Sb <sub>2</sub> O <sub>3</sub>	5
Example 12	Syndiotactic	50	0.49	50	a	12	Sb <sub>2</sub> O <sub>3</sub>	3
Example 13	Syndiotactic	50	0.49	50	a	12	Sb <sub>2</sub> O <sub>3</sub>	3
Example 14	Syndiotactic	50	0.49	50	c	16	Sb <sub>2</sub> O <sub>3</sub>	4
Example 15	Syndiotactic	50	0.49	50	a	16	Sb <sub>2</sub> O <sub>3</sub>	4
Example 16	Syndiotactic	75	0.49	25	a	30	Sb <sub>2</sub> O <sub>3</sub>	8
Example 17	Syndiotactic	50	0.49	50	a	16	Sb <sub>2</sub> O <sub>3</sub>	4
Comparative Example 13	Atactic	50	0.49	50	a	12	Sb <sub>2</sub> O <sub>3</sub>	3
Example 18	Syndiotactic	90	0.49	10	a	24	Sb <sub>2</sub> O <sub>3</sub>	6

Table 4 (continued)

No.	Component E				Flame Retardance Test	
	Rubber- like elastomer	*5 part by weight	*4 Inorganic filler	*5 part by weight	UL 94	Thickness (Inch)
Example 10	-	-	-	-	V-0	1/32
Comparative Example 12	-	-	-	-	V-0	1/32
Example 11	-	-	talc	15	V-0	1/32
Example 12	-	-	CaCO <sub>3</sub>	15	V-0	1/32
Example 13	-	-	GF	43	V-0	1/32
Example 14	SB	15	-	-	V-0	1/32
Example 15	MAS	15	-	-	V-0	1/32
Example 16	MAS	40	GF	75	V-0	1/32
Example 17	SB	15	talc	15	V-0	1/32
Comparative Example 13	-	-	-	-	V-0	1/32
Example 18	-	-	GF mica	130 65	V-0	1/32

\*1 Styrene-based polymer

Syndiotactic: Polystyrene having syndiotactic  
configuration, obtained in Reference  
Example 1

Atactic: Idemitsu Polystyrene US305, produced by  
Idemitsu Petrochemical Co., Ltd.

\*2 PPE resin: Polyphenylene ether resin obtained in  
Reference Example 2

\*3 Flame retarder

a: Polytribromostyrene ... Pyrocheck 68 PB, produced by  
Nissan Ferro Co.

b: Decabromodiphenyl ether ... Trade Name: SAYTEX 102,  
produced by Ethyl Corporation

c: Poly(dibromophenylene oxide) ... GLC PO-64P, produced  
by Great Lakes, Ltd.

\*4 Proportion to the total amount of Component A and  
Component B as 100 parts by weight

\*5 Rubber-like elastomer

SB: Styrene-grafted butadiene rubber (particle diameter:  
0.7  $\mu$ m, Name of Product on an trial basis: Metablen  
IP-2, produced by Mitsubishi Rayon Co., Ltd.)

MAS: Methyl methacrylate - n - butyl acrylate - styrene  
copolymer (Trade Name: KM 330, produced by Rohm &  
Haas Company)

## \*6 Inorganic filler

GF: Glass fiber (Length of fiber: 3 mm, Diameter: 13

μm, CS03 MA 429A, produced by Asahi Fiber Glass  
Co., Ltd.)

talc: (Average particle diameter: 0.6 μm, Talc FFR,  
produced by Asada Seifun Co.)

CaCO<sub>3</sub>: Calcium carbonate having average particle diameter  
of 2 μm

Table 5

No.	Tensile Fracture elongation (%)	Bending strength (kg/cm )	Gasoline-Dipping Test *1
Example 10	4	1470	A
Comparative Example 12	1	980	A
Example 11	4	1260	A
Example 12	5	1250	A
Example 13	5	1600	A
Example 14	20	1060	A
Example 15	18	1070	A
Example 16	16	1520	A
Example 17	16	1070	A
Comparative Example 13	3	1290	C
Example 18	-	1730	A

\*1 Left for one week at room temperature

A ... No change in appearance

B ... Swollen (not less than 10% of increase in weight)

C ... Dissolved

Table 6

No.	Intrinsic viscosity of PPE (dl/g)	SPS/PPE Ratio (by weight)	Way of stretching	Temp. of stretching (°C)	Draw ratio (times)	Annealing *	Tensile strength (kg/mm <sup>2</sup> )	Elongation at break (%)	Tensile modulus (kg/cm <sup>2</sup> )
Example 19	0.32	95/5	Uniaxially	120	4	No	20	25	144000
Example 20	0.32	95/5	Uniaxially	120	2	No	17	10	125000
Example 21	0.32	95/5	Uniaxially	120	4	Done	21	25	148000
Comparative Example 14	0.32	99/1	Uniaxially	120	4	No	15	4	133000
Example 22	0.32	80/20	Uniaxially	120	4	No	22	28	154000
Example 23	0.32	80/20	Biaxially	120	3.5x3.5	No	15	14	53000
Example 24	0.32	80/20	Biaxially	120	3.5x3.5	Done	15	14	54000
Example 25	0.49	50/50	Biaxially	170	3.5x3.5	No	20	17	52000
Example 26	0.49	15/85	Biaxially	190	3.5x3.5	No	22	20	50000
Comparative Example 15	0.49	5/95	No sheet formed	-	-	-	-	-	-
Notes:									

\* Conditions for annealing: 250 °C, 30 seconds

## Claims

5

1. A styrene-based polymer composition which comprises
  - (A) 10 to 98% by weight of a styrene-based polymer having syndiotactic configuration with a racemic pentad of 30% or more and
  - (B) 90 to 2% by weight of a polyphenylene ether having an intrinsic viscosity of 0.28 dl/g or more at 30° C in chloroform.
- 10 2. A styrene-based polymer composition which comprises
  - (A) 10 to 98% by weight of a styrene-based polymer having syndiotactic configuration with a racemic pentad of 30% or more and
  - (B) 90 to 2% by weight of PPE having an intrinsic viscosity of 0.28 dl/g or more at 30° C in chloroform, and
  - (C) 3 to 40 parts by weight of a flame retarder and
  - (D) 1 to 15 parts by weight of a flame-retardant aid based on 100 parts by weight of the total amount of (A) and (B).
- 20 3. A styrene-based polymer composition which comprises
  - (A) 10 to 98% by weight of a styrene-based polymer having syndiotactic configuration with a racemic pentad of 30% or more and
  - (B) 90 to 2% by weight of a polyphenylene ether having an intrinsic viscosity of 0.28 dl/g or more at 30° C in chloroform, and
  - (E) 5 to 85 parts by weight of a rubber-like elastomer or 1 to 250 parts by weight of an inorganic filler based on 100 parts by weight of the total amount of (A) and (B).
- 25 4. A styrene-based polymer composition which comprises
  - (A) 10 to 98% by weight of a styrene-based polymer having syndiotactic configuration with a racemic pentad of 30% or more and
  - (B) 90 to 2% by weight of a polyphenylene ether having an intrinsic viscosity of 0.28 dl/g or more at 30° C in chloroform, and
  - (E) 5 to 85 parts by weight of a rubber-like elastomer and 1 to 250 parts by weight of an inorganic filler based on 100 parts by weight of the total amount of (A) and (B).
- 30 5. A styrene-based polymer composition which comprises
  - (A) 10 to 98% by weight of a styrene-based having syndiotactic configuration with a racemic pentad of 30% or more and
  - (B) 90 to 2% by weight of PPE having an intrinsic viscosity of 0.28 dl/g or more at 30° C in chloroform, and
  - (C) 3 to 40 parts by weight of a flame retarder,
  - (D) 1 to 15 parts by weight of a flame-retardant aid and
  - (E) 5 to 85 parts by weight of a rubber-like elastomer or 1 to 250 parts by weight of an inorganic filler based on 100 parts by weight of the total amount of (A) and (B).
- 40 6. A styrene-based polymer composition which comprises
  - (A) 10 to 98% by weight of a styrene-based having syndiotactic configuration with a racemic pentad of 30% or more and
  - (B) 90 to 2% by weight of PPE having an intrinsic viscosity of 0.28 dl/g or more at 30° C in chloroform, and
  - (C) 3 to 40 parts by weight of a flame retarder,
  - (D) 1 to 15 parts by weight of a flame-retardant aid and
  - (E) 5 to 85 parts by weight of a rubber-like elastomer and 1 to 250 parts by weight of an inorganic filler based on 100 parts by weight of the total amount of (A) and (B).
- 50 7. A styrene-based polymer composition according to any one of Claims 2, 5 and 6, wherein the flame retarder of said component (C) is at least one compound selected from decabromodiphenyl ether, polytribromostyrene and poly(dibromophenylene oxide).
8. A styrene-based polymer composition according to any one of Claims 2, 5 and 6, wherein the flame-retardant aid of said component (D) is antimony trioxide.
- 55 9. A styrene-based polymer composition according to any one of Claims 3 to 6, wherein the rubber-like elastomer of said component (E) is a rubber-like elastomer containing a styrene-based compound as a partial component thereof.

10. A styrene-based polymer composition according to any one of Claims 3 to 6, wherein the inorganic filler of said component (E) is glass fiber.

11. A stretched molding which comprises stretching the styrene-based polymer composition of Claim 1.

12. A stretched molding according to Claim 11, wherein a draw ratio at least in uniaxially stretching is at least 1.5 times.

13. A stretched molding according to Claim 11, wherein a draw ratio in biaxially stretching is at least 1.2 times in each direction.

14. A process for producing a stretched molding which comprises heat melting the composition of Claim 1, cooling the resultant molten composition to a temperature lower than a temperature 30 °C above the glass transition temperature of the composition to form a raw sheet, and then subjecting the sheet to stretching treatment with heating to a temperature between the glass transition temperature and a melting point of the composition.

15. A process for producing a stretched molding which comprises subjecting the molding of Claim 11 to annealing at a temperature between 100 °C and the melting point of the composition.

(19)



Europäisches Patentamt  
European Patent Office  
Office européen des brevets

(11) Publication number:

**0 356 857**  
**A3**

(12)

## EUROPEAN PATENT APPLICATION

(21) Application number: **89115354.6**(22) Date of filing: **19.08.89**

(51) Int. Cl.<sup>5</sup>: **C08L 25/06, C08L 71/12,**  
**B29C 55/00, C08J 5/18,**  
**/(C08L25/06,71:12),**  
**(C08L71/12,25:06)**

(30) Priority: **31.08.88 JP 215095/88**  
**30.09.88 JP 244581/88**  
**30.09.88 JP 244583/88**

(43) Date of publication of application:  
**07.03.90 Bulletin 90/10**

(84) Designated Contracting States:  
**AT BE CH DE ES FR GB IT LI NL SE**

(88) Date of deferred publication of the search report:  
**16.08.90 Bulletin 90/33**

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(54) **Styrene-based polymer composition, stretched molding thereof and process for producing the same.**

(57) There is disclosed a styrene-based polymer composition which comprises

(A) 10 to 98% by weight of a styrene-based polymer having syndiotactic configuration with a racemic pentad of 30% or more and

(B) 90 to 2% by weight of polyphenylene ether having an intrinsic viscosity of 0.28 dl/g or more at 30°C in chloroform.

Also, a flame retarder, a flame-retardant aid, a rubber-like elastomer or an inorganic filler may optionally be added to the composition.

Further, also disclosed is a stretched molding comprising stretching the above composition.

**EP 0 356 857 A3**



European Patent  
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## EUROPEAN SEARCH REPORT

Application Number

EP 89 11 5354

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The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-05-1990	Examiner DE LOS ARCOS Y VELAZQUEZ
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X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	